RESTRICTED MASS TRANSPORT EFFECTS ON FREE RADICAL REACTIONS

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INTRODUCTION

Research aimed at the development of improved coal utilization technologies such as coal liquefaction and hydropyrolysis continue to benefit from the insights provided by well-designed model compound studies[1]. The importance of controlling hydrogen utilization in the development of economically competitive processes is well-recognized. The donation of hydrogen atoms to a reactive site in coal, such as a free radical, can occur from molecules native to the coal structure, hydrogen gas, or a liquefaction donor solvent. The hydrogen transfer can also be mediated by the presence of a catalyst. Model compound studies continue to probe the mechanisms of hydrogen transfer and utilization potentially involved in coal liquefaction.[1]

Coal possesses a complex chemical and physical structure. The cross-linked, network structure can lead to alterations in normal thermally-induced, free-radical decay pathways as a consequence of restrictions on mass transport. Moreover, in coal liquefaction, access of an external hydrogen donor to a reactive radical site can be hindered by the substantial domains of microporosity present in coals.[2,3] Larsen et al. have recently investigated the short contact time liquefaction of Illinois No. 6 coal in the presence of either tetralin or 2-*tert*-butyltetralin as the hydrogen donor solvent.[2] Remarkably, both the yields of pyridine extractables and the amount of hydrogen transferred from the donor solvent are the same despite the presence of the bulky *tert*-butyl group. Diffusion effects do not appear to be playing an important role in this coal conversion chemistry. Several possible explanations for this phenomenon were advanced including the potential involvement of a hydrogen hopping/radical relay mechanism recently discovered in model systems in our laboratories.[4,5]

We have employed silica-anchored compounds to explore the effects of restricted mass transport on the pyrolysis mechanisms of coal model compounds.[4-7] In studies of two-component systems, cases have been discovered where radical centers can be rapidly relocated in the diffusionally constrained environment as a consequence of rapid serial hydrogen atom transfers. This chemistry can have substantial effects on thermal decomposition rates[4] and on product selectivities.[5] In this study, we examine additional surfaces to systematically investigate the impact of molecular structure on the hydrogen atom transfer promoted radical relay mechanism. Silica-attached 1,3-diphenylpropane ($\approx$Ph(CH$_2$)$_3$Ph, or $\approx$DPP) was chosen as the thermally reactive component, since it can be considered prototypical of linkages in coal that do not contain weak bonds easily cleaved at coal liquefaction temperatures (ca. 400°C), but which crack at reasonable rates if benzylic radicals can be generated by hydrogen abstraction. The rate of such hydrogen transfers under restricted diffusion will be highly dependent on the structure and proximity of neighboring molecules.[4,7]

EXPERIMENTAL

The two-component surfaces shown below were synthesized from the corresponding phenols by co-reaction with the surface hydroxyls of a nonporous, fumed silica (surface area of 200 ± 25 m^2/ g) as previously described.[4-7] The compounds are covalently anchored to the silica surface by a thermally robust Si-O-C$_{aryl}$ linkage. The resulting two-component surfaces had purities of ≥ 99.3%.
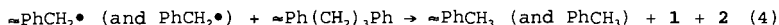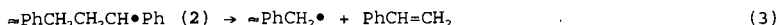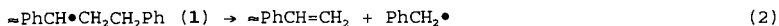
Pyrolyses were performed in sealed, evacuated (2 x 10^{-6} torr), T-shaped tubes at 375°C. During the reaction, any volatile materials formed migrated out of the heated zone and were collected in the sidearm cold trap (77K). After the reaction, the volatile products in the trap were dissolved in acetone and analyzed by GC and GC-MS with the use of internal calibration standards. Base hydrolysis (1N NaOH) of the silica residue liberated the surface-attached

products and unreacted starting materials, which were isolated as the corresponding phenols following neutralization and extraction with CH_2Cl_2. These products were silylated with N,O-bis(trimethylsilyl)trifluoroacetamide in pyridine (2.5M), and the corresponding trimethylsilyl ethers were analyzed in the presence of internal standards by GC and GC-MS.

~~ DPP / ~~ BP   ~~ DPP / ~~ NAP   ~~ DPP / ~~ DPM

~~ DPP / ~~ DPM-d$_2$ ~~ DPP / ~~ m-DPM

~~ DPP / ~~ FL   ~~ DPP / ~~ DHP
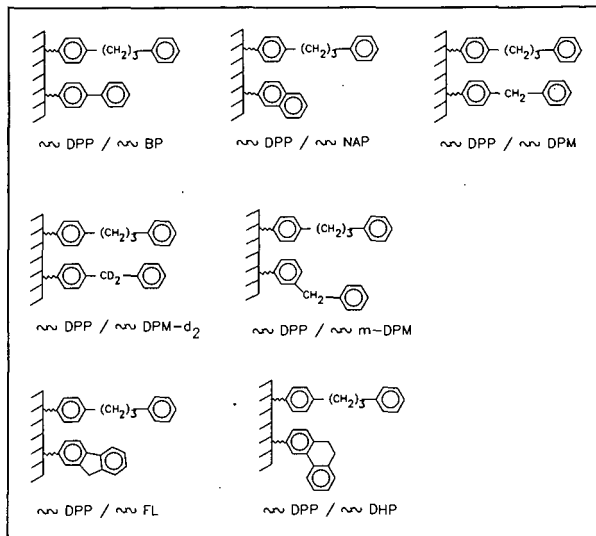
RESULTS AND DISCUSSION

If the rate of decomposition of 1,3-diphenylpropane were governed solely by homolysis of its weakest bond (about 74 kcal/mol) to form $PhCH_2\bullet$ and $\bullet CH_2CH_2Ph$, then DPP would be stable at 400°C with a half life on the order of 19 years.[8] The fact that DPP is thermally reactive even at 375°C derives from the incursion of a free-radical chain decomposition pathway that produces benzylic radicals capable of cracking by β-scission. For silica-immobilized DPP ($\approx$DPP), this reaction produces the cracking products shown in Eq. 1 with the radical chain propagation steps shown in Eqs. 2-4.[7] As shown in Table 1, the rate of $\approx$DPP decomposition decreases substantially with decreasing surface coverage as the rate for the hydrogen atom transfer step 4 decreases. This should be particularly important

$$\approx Ph(CH_2)_3Ph \rightarrow PhCH_3 + \approx PhCH=CH_2 + \approx PhCH_3 + PhCH=CH_2 \tag{1}$$

$$\approx PhCH\bullet CH_2CH_2Ph\ (1) \rightarrow \approx PhCH=CH_2 + PhCH_2\bullet \tag{2}$$

$$\approx PhCH_2CH_2CH\bullet Ph\ (2) \rightarrow \approx PhCH_2\bullet + PhCH=CH_2 \tag{3}$$

$$\approx PhCH_2\bullet\ (and\ PhCH_2\bullet) + \approx Ph(CH_2)_3Ph \rightarrow \approx PhCH_3\ (and\ PhCH_3) + 1 + 2 \tag{4}$$

for hydrogen abstraction by the surface-attached benzyl radical, $\approx PhCH_2\bullet$, as the spatial separation between reactants increases with decreasing surface coverage. Similar rate decreases are observed in pyrolysis of liquid-phase DPP when the concentration is decreased by dilution with an inert solvent.

Discovery of the radical relay mechanism originated from studies of the pyrolysis of the surfaces, $\approx$DPP/$\approx$BP, $\approx$DPP/$\approx$NAP, and $\approx$DPP/$\approx$DPM, where the biphenyl and naphthalene spacers were innocuous, but the diphenylmethane spacer molecules resulted in greatly enhanced decomposition rates (ca. 10-fold) for $\approx$DPP when compared at similar surface coverages of $\approx$DPP (see Table 1).[4] This is in contrast to liquid phase DPP pyrolyses where DPM behaves as other inert diluents.[4] In the surface-immobilized cases, no new products were formed, and the involvement of diphenylmethane moieties in the relay pathway was confirmed from the study of $\approx$DPP/$\approx$DPM-d$_2$. In addition to an apparent deuterium isotope effect on the reaction rate, incorporation of substantial amounts of deuterium in the vapor-phase and surface-attached toluene products was detected. A pictorial representation of the radical relay process is shown below. The facility of this process, which leads to rates
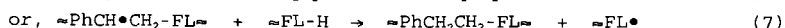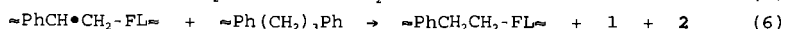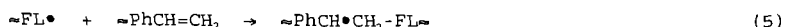
comparable to saturated coverages of ≈DPP without spacer molecules, is likely a consequence of enhanced A-factors for the bimolecular hydrogen transfer steps on the surface for these "pre-organized" reactants. Similar effects have been proposed to explain the enhanced rates often observed for organic reactions on clay surfaces, which are attributed to a "reduction in the dimensionality of the reaction space".[9]

Table 1. Effect of Spacer Structure on Pyrolysis of ≈DPP at 375°C		
Surface Composition	Coverage (mmol g^{-1})	Rate x 10^4 (% s^{-1})
≈DPP	0.59	24.0
	0.14	1.1
	0.10	0.72
≈DPP / ≈BP	0.13 / 0.51	2.2
≈DPP / ≈NAP	0.12 / 0.44	1.9
≈DPP / ≈DPM	0.17 / 0.42	21.0
	0.13 / 0.37	17.0
≈DPP / ≈DPM-d$_2$	0.16 / 0.36	12.0
≈DPP / ≈m-DPM	0.17 / 0.31	27.0
≈DPP / ≈FL	0.17 / 0.42	86.0
≈DPP / ≈DHP	0.21 / 0.36	8.6
	0.065 / 0.47	13.0
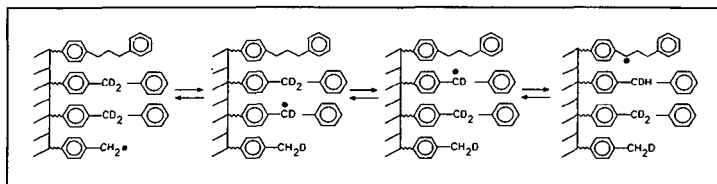
As shown in Table 1, the use of the isomeric *meta*-diphenylmethane spacer similarly produces enhanced rates, and appears even more effective than the *para*-analog at participating in the radical relay process. The fluorene spacer (≈FL) is a cyclic analog to ≈m-DPM, which is known to have faster kinetics for hydrogen donation to benzyl radicals because it does not require phenyl rotations to be frozen in the transition state.[8] However, in the surface-attached analog, the fact that the benzylic hydrogens are attached to a carbon locked in a ring could potentially lead to geometrical constraints in the hydrogen transfer steps on the surface. As shown in Table 1, the ≈DPP pyrolysis rate is substantially enhanced in the presence of ≈FL compared even with the DPM cases. However, for ≈DPP/≈FL, we have found that the majority of the ≈PhCH=CH$_2$ product has undergone reaction with fluorenyl radical in a chain transfer step (Eq. 5). The resulting radical does not terminate the chain, but abstracts hydrogen to provide an additional pathway for relaying radical centers on the surface (Eq. 6 and 7). This additional pathway apparently also contributes to the facile decomposition of ≈DPP.

$$≈FL• \; + \; ≈PhCH=CH_2 \; \rightarrow \; ≈PhCH•CH_2-FL≈ \tag{5}$$

$$≈PhCH•CH_2-FL≈ \; + \; ≈Ph(CH_2)_3Ph \; \rightarrow \; ≈PhCH_2CH_2-FL≈ \; + \; 1 \; + \; 2 \tag{6}$$

$$or, \; ≈PhCH•CH_2-FL≈ \; + \; ≈FL-H \; \rightarrow \; ≈PhCH_2CH_2-FL≈ \; + \; ≈FL• \tag{7}$$

The hydroaromatic, 9,10-dihydrophenanthrene (DHP), is often employed as a model hydrogen donor liquefaction solvent. It can be seen from Table 1 that ≈DPP reacts faster in the presence of co-attached DHP (≈DHP) than in the presence of the inert aromatics, biphenyl (≈BP) and naphthalene (≈NAP), although not as fast as in the presence of ≈DPM. The radical relay chemistry is more

complicated with ≈DHP, however, because chain propagation can also occur via hydrogen atoms donated by the intermediate hydrophenanthryl radicals, ≈DHP•, which would not experience diffusional constraints (Eqs. 8 and 9). Consistent with this premise, we observe formation of modest amounts of surface-attached phenanthrene (≈PHEN), as well as new products resulting from hydrocracking of ≈DPP (accounting for ca. 2% of the reacted ≈DPP) to form ≈PhH + PhC_3H_7 and PhH + ≈PhC_3H_7. However, it is interesting that the ≈DPP decomposition rate is substantially greater for the diphenylmethane spacers which serve only as radical relay catalysts.

$$≈DHP• \rightarrow ≈PHEN + H• \tag{8}$$

$$H• + ≈Ph(CH_2)_3Ph \rightarrow H_2 + \mathbf{1} + \mathbf{2} \tag{9}$$

CONCLUSIONS

This study shows that the rate at which surface-immobilized 1,3-diphenylpropane thermally decays at 375°C can span a substantial range that is dependent on the structure of neighboring molecules on the surface. It seems clear that it is possible for radical centers to relocate in diffusionally constrained environments at relevant coal liquefaction temperatures, without the need for physical movement, by means of rapid serial hydrogen atom transfers. There may exist an optimum set of chemical structures that possess the appropriate thermochemical and structural properties to promote the radical relay phenomenon under conditions of restricted diffusion, and we continue to explore additional spacer molecules.

The significance of these results for coal liquefaction encompasses two points. If the cleavage of a linkage embedded in a microporous domain in coal requires formation of a radical precursor (as typified by DPP in the current study), then a radical relay mechanism could transfer that needed "reactivity" to the linkage in question. Alternatively, if a radical is formed in an inaccessible region of the coal network and needs to be capped by a hydrogen source to prevent a retrogressive reaction, then a radical relay pathway could relocate the radical center to a region in the coal that is accessible to a hydrogen donor in the liquefaction medium. It remains to be determined whether such a phenomenon contributes to the coal liquefaction behavior recently reported by Larsen (*vide supra*).[2]

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